Supporting Information

Co_3C as a Promising Cocatalyst for Superior Photocatalytic H_2 Production Based on Swift Electron Transfer Process

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2. Experimental

2.1. Materials

All the chemicals and reagents, including cobalt chloride ($CoCl_2$, 98%), tetraethylene glycol ($C_6H_{14}O_4$, 99%), cadmium chloride hemipentahydrate ($CdCl_2 \cdot 2.5H_2O$, 99.0%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 99.0%) anhydrous sodium sulfate (Na_2SO_3, 99.0%) and thiourea (CH_4N_2S, 99.0%), were purchased from Sigma Aldrich and used without further purification.

2.2. Synthesis of cocatalysts and photocatalysts

The highly efficient Co_3C was prepared using a reported method.[1] Obtained Co_3C was further used to prepare composite photocatalysts. Typically, 101 mg of CdS NRs were added to a 50 mL flask containing 10 mL ethanol followed by the addition of calculated amount (3 mg, 6 mg, 12 mg, 25 mg and 50 mg) of Co_3C. The flask was sealed and purged with N_2 for 15 min to remove the air. The suspension was well dispersed using ultrasonication for 30 min. The sample was dried at 80 °C under vacuum. The obtained sample was gently ground in an agate mortar for 15 min and then annealed at 200 °C under Ar. The prepared samples were labeled as CC1, CC2, CC3, CC4 and CC5. For comparative study, similar process was performed with pure CdS NRs. Pt/CdS NRs photocatalyst was obtained through loading of 1 wt% Pt on pristine CdS NRs by a reported procedure.[2]

2.3. Photocatalytic H_2 production

The Photocatalytic activities of photocatalytic samples for H_2 production were explored in 50 mL round bottom flask under visible light. For visible light irradiation, a 300 W Xe lamp equipped with 420 nm cut-off filter was used. The photocatalytic reaction mixtures were prepared in 20 mL Millipore water having 2.0 mg photocatalyst, Na_2S/Na_2SO_3 as sacrificial

reagent. Air from the reaction mixture was removed by N_2 purging for 15 min and 5 mL methane was added as internal standard. H_2 gas resulted from photocatalytic sample was quantified by gas chromatography (GC, SP-6890, N_2 as carrier gas) equipped with thermal conductivity detector (TCD). A monochromatic light (420 nm) was employed for apparent quantum yields (AQYs) and calculations were performed according to the following equation:

$$AQY\ (\%) = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100$$

$$= \frac{number\ of\ evolved\ H_2 molecules\ \times 2}{number\ of\ incident\ photons} \times 100 \qquad (1)$$

2.4. Photoelectrochemical studies

Photocurrent performance of the photocatalytic samples was studied using a CHI602E work station (Shanghai Chenhua Instrument Co., Ltd, Shanghai, China). A standard three-electrode system was established using photocatalyst-coated FTO as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. Visible light irradiation was provided with a 300 W Xe lamp equipped with 420 nm cut-off filter. Working electrodes were prepared by adding 15 μL suspensions of CdS and Co_3C/CdS NRs (20 mg/mL) onto the surface of FTO and dried at room temperature. For measurements, an applied potential of 0 V vs Ag/AgCl was used in 0.5 M Na_2SO_4 aqueous solution as electrolyte. The polarization curves were measured using linear sweep voltammetry (LSV) with a scan rate of 5 mV/s.

2.5. Characterization

Morphologies of the samples were studied on scanning electron microscopy (SEM) using a JSM-6700F microscope. Transmission electron microscopy **(**TEM) and energy-dispersive X-ray analysis (EDX) analysis were obtained on the transmission electron microscope JEM-2010

equipped with a Rontec EDX system and electron diffraction (ED) attachment with an acceleration voltage of 200 kV. Powder X-ray diffraction analysis of the compounds was done on (XRD, D/max-TTR III) using graphite monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min^{-1} from 20° to 80° in 2θ. XPS studies were performed on an ESCALAB 250 X-ray photoelectron spectrometer. ICP-AES (Optima 7300 DV) was used for the measurement of cobalt contents in photocatalysts. The steady-state photoluminescence (PL) spectra were obtained using a Perkin-Elmer LS 55 fluorescence spectrometer. UV-vis diffuse reflectance was performed on a Solid Spec-3700 UV-vis spectrometer. Time-resolved photoluminescence (TRPL) spectra were obtained on a PicoHarp 300 (PicoQuant) TRPL spectrometer.

Table S1. ICP-AES data of Co_3C/CdS samples.

Sample	Co (wt%)/ ICP-AES data
CC1	2.23
CC2	5.18
CC3	11.67
CC4	24.31
CC5	48.74

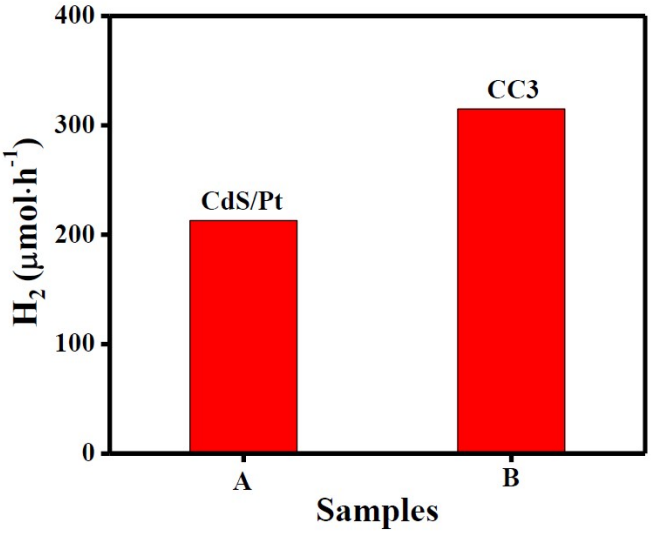


Figure S1. Comparison of photocatalytic performance of CdS NR loaded with Pt and CC3 using 2 mg photocatalyst in 20 mL Millipore water containing 1.0 M Na_2S and 1.40 M Na_2SO_3.

Table S2. Comparison of photocatalytic performance of carbides/CdS based photocatalytic systems. For better comparison, data was converted to mmol h^{-1} g^{-1}.

Sr. No.	Photocatalyst	Rate (mmol h^{-1} g^{-1})	AQY (%)	Reference
1	CdS/WC	1.35	----	[3]
2	CdS/Ni_3C	18.2	8.72 (420 nm)	[4]
3	CdS/Ti_3C_2 Mxene	14.34	40.1 (420 nm)	[5]
4	CdS/VC	14.2	8.7 (420 nm)	[6]
5	CdS/Mo_2C	1.61	3.41 (420 nm)	[7]
6	CdS/Co_3C	15.75	19 (420 nm)	Present work

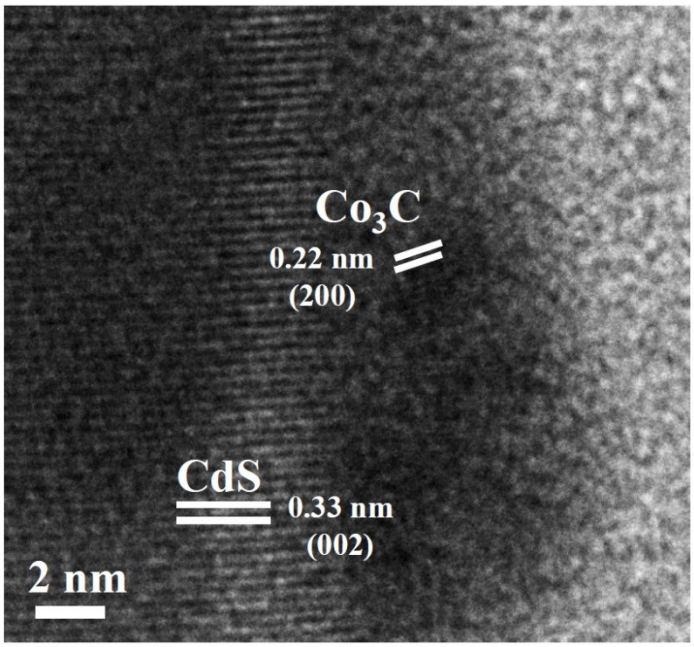


Figure S2. HRTEM image of CC3.

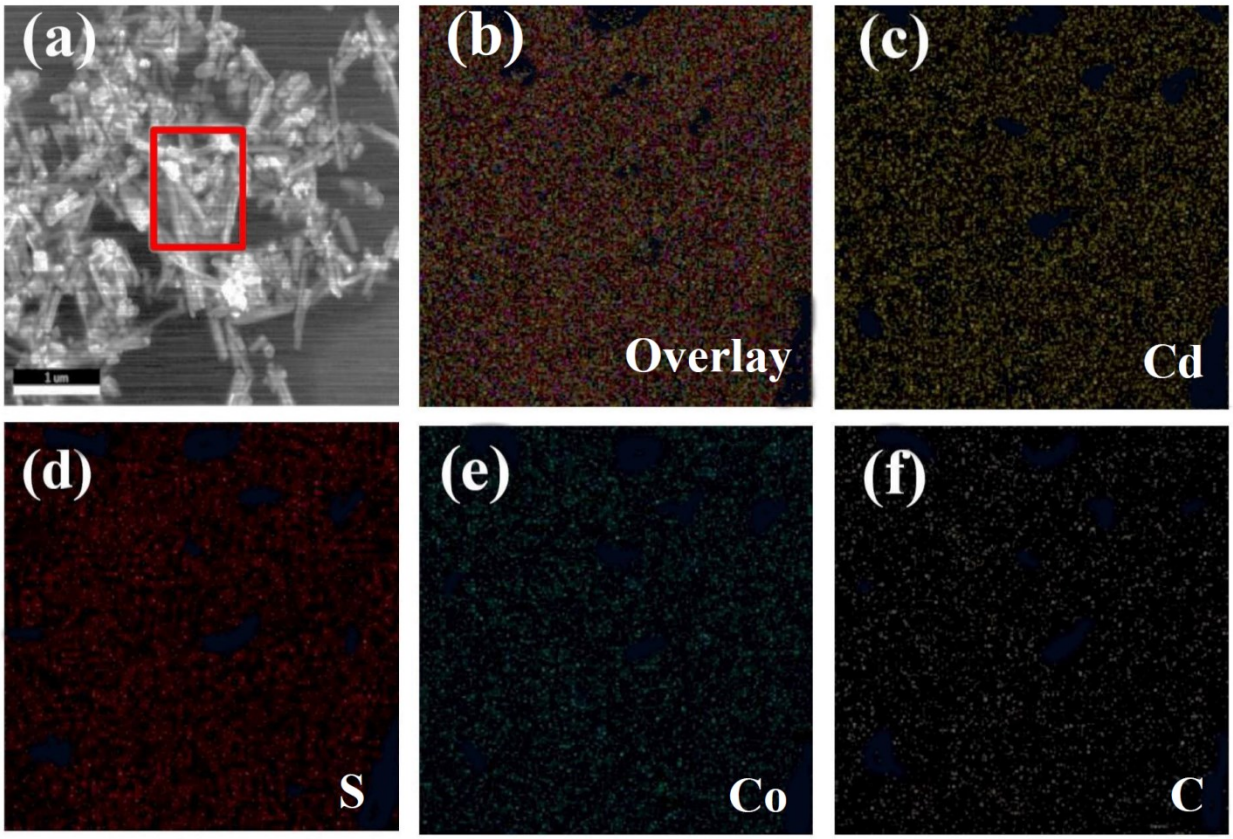


Figure S3. EDS elemental mapping images of CC3.

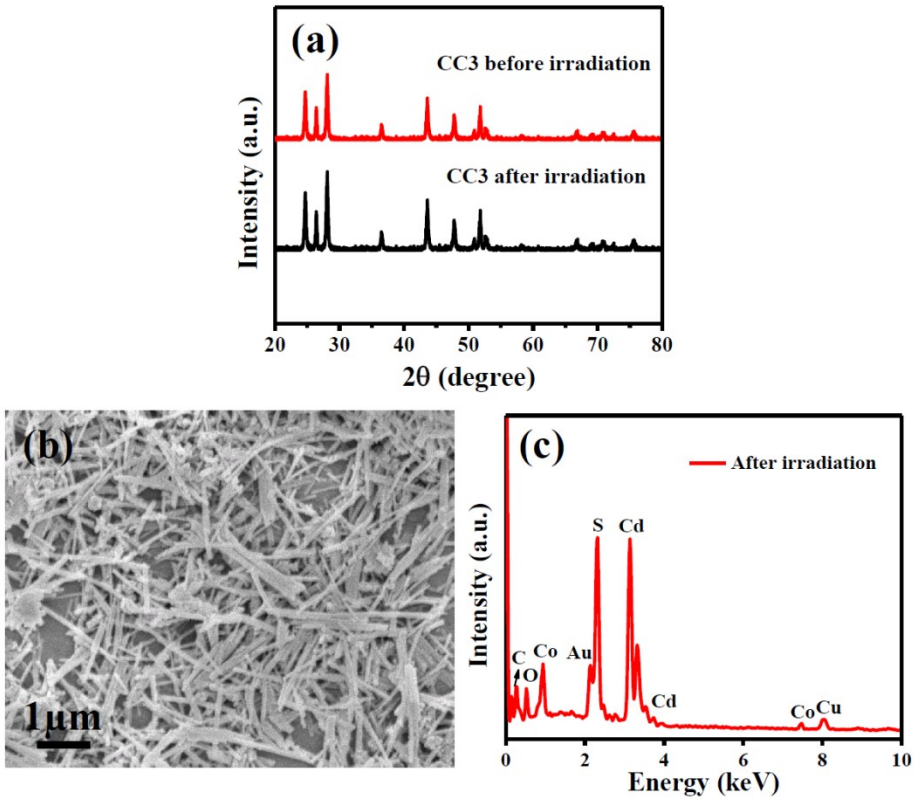
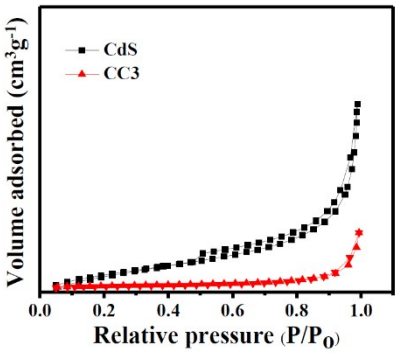


Figure S4. **(a)** XRD patterns of CC3 before (red plot) and after (black plot) irradiation. **(b)** SEM image of CC3 after irradiation. **(c)** EDX spectrum of CC3 after irradiation.



Entry	Catalyst	Surface area (S_{BET}) ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)
1	CdS	24.46	0.11
2	CC3	13.49	0.045

Figure S5. Nitrogen adsorption–desorption isotherms and corresponding pore-size distribution curves

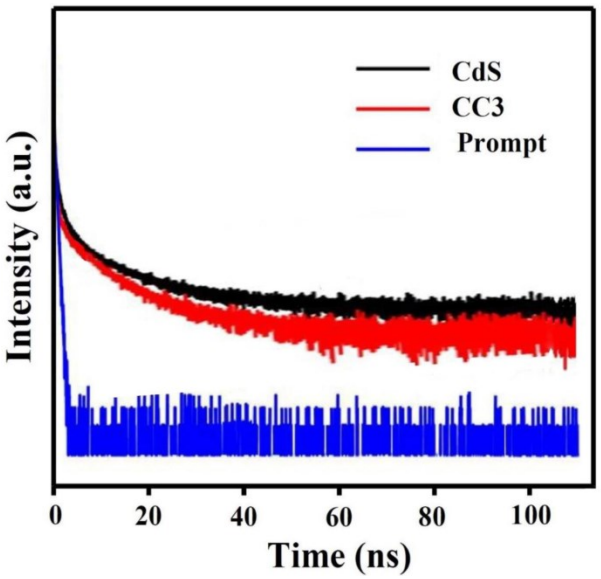


Figure S6. Time-resolved photoluminescence (TRPL) spectra of CdS NRs, and Co_3C/CdS NRs at an excitation wavelength of 405 nm.

References

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